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ORGANOMETALLIC LIQUIDS AS POTENTIAL DOSIMETRIC MATERIALS: A PULSE RADIOLYSIS STUDY OF THE TETRAETHYL COMPOUNDS OF Si, Ge, Sn AND Pb

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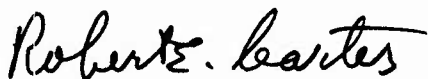ORGANOMETALLIC LIQUIDS AS POTENTIAL DOSIMETRIC MATERIALS:

A PULSE RADIOLYSIS STUDY OF THE TETRAETHYL

COMPOUNDS OF Si, Ge, Sn AND Pb

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TABLE OF CONTENTS

LIST OF FIGURES

FOREWORD
(Nontechnical summary)

There exists a continuing requirement for the development of dosimetry systems to be used in pulsed fields of ionizing radiation, particularly low-energy x radiation. A preferred dosimeter would be capable of live time readout to follow pulse profiles over a time scale of several nanoseconds. It also would be responsive to the spectral distribution of the x rays, i.e., able to discriminate between photons of different energies.

A homologous series of organometallic liquids, the tetraethyl compounds of silicon, germanium, tin and lead, are being considered for this purpose. Each member of the series contains one metal atom per molecule which absorbs energy preferentially in different regions of the x-ray spectrum. Little is known, however, about the radiation chemistry of this class of materials, particularly with regard to any induced change in physical properties that could be readily recognized and measured within the desired time range.

This phase of the investigation was undertaken to assess the potential of these organometallic substances as dosimetric materials by first gaining a better understanding of the radiolytic processes. The methods of fast reaction kinetics have been employed to observe the formation and decay of transient optical absorption spectra in each compound. The reactive intermediates responsible for the transient spectra were monitored for several hundred microseconds following a pulse of radiation. They have been tentatively identified as trialkyl-metal free radicals arising from rupture of the carbon to metal chemical bonds.

ABSTRACT

The methods of kinetic optical spectroscopy have been employed to observe the formation and decay of short-lived transients produced by pulse radiolysis of the tetra-alkyl compounds of the Group IVA metals. Time resolved transient spectra over the range of 290 nm to 620 nm are presented. The probable mechanisms of the radiation-induced molecular disruption are considered and the feasibility of utilizing these compounds as dosimeters in the low-energy x-ray region is discussed.

I. INTRODUCTION

With the development of pulse radiolysis techniques,[15] it is now often possible to identify short-lived chemical intermediates produced by a single burst of ionizing radiation in a target material. The kinetics and mechanisms of the induced reactions may be studied by observation of one or more of the physical properties of these transient species. In irradiated water, for example, one of the major radiolysis products is the hydrated electron e_{aq}^-. The properties and reactions of this highly reactive entity have been thoroughly studied in recent years and much is now known about its optical properties. It possesses an intense optical absorption with a maximum near 700 nm and thus can be readily monitored. Since the concentration of e_{aq}^- immediately following a pulse of radiation is proportional to absorbed dose, spectral measurements at a defined wavelength afford a valuable means of conducting pulsed radiation dosimetry.

An important contribution in the field of pulse dosimetry has been made by Klein et al.[10] Using dilute aqueous solutions as target material and the optical absorption of e_{aq}^-, the system they describe is capable of live time readout and of determining pulse profiles for pulses as short as 10 nanoseconds. Klein et al. also have demonstrated the feasibility of using radiation filters to provide spectral discrimination when the method is applied to the dosimetry of low-energy x rays. Clearly this idea can be extended to utilize a series of irradiation cells, each containing a different target material and absorbing preferentially at a specific energy, e.g., at the K-edge of a medium-Z element. A simple illustrative example utilizing two cells is given in Appendix A.

1

The practical application of an x-ray K-edge spectrometry system depends on the availability of cell liquids with appropriate energy absorbing properties, i.e., the ratio of photoelectric to Compton energy absorption must be large. The number of medium or high-Z atoms should be at least equal to the number of low-Z carrier molecules. To achieve this ratio in aqueous solutions would require impractically high solute concentrations. There are many organometallic compounds, however, that satisfy these conditions.

The purpose of this investigation was to undertake a pulse radiolysis study of several organometallic liquids, primarily to learn whether or not one can produce transient chemical species with well-defined optical absorption spectra. The target materials initially selected for examination are some of the tetra-alkyl compounds of the Group IV elements, silicon, germanium, tin and lead. These are all stable, transparent liquids of low volatility and are readily available. There is a limited background of information on the radiation chemistry of these compounds and much of this is covered in a review of the subject by Blackburn and Kabi.[2] A more complete understanding of the mechanisms of radiolysis is clearly desirable at this point. Mass spectrometric studies of some simple silicon, tin and germanium compounds[6,11] indicate the nature and reactions of the free radical and ionic intermediates to be expected in radiolysis. A preliminary pulse radiolysis investigation of triethyl aluminum in diethyl ether solution[12] has shown the presence of reactive transient species in irradiated material, with optical absorption spectra in the region of 300 nm.

II. EXPERIMENTAL

Irradiation procedures. The AFRRI electron linear accelerator (LINAC) was used as a pulsed source of ionizing radiation. All organometallic liquids were exposed to single pulses of 40 MeV electrons, each of 200-nsec duration and selected from a 10 percent beam energy bin. Changes in optical absorption of the irradiated material were examined by the methods of pulse radiolysis and kinetic spectroscopy. [15] The basic experimental arrangement for detection of transient absorption spectra is shown in Figure 1. Light from a xenon arc lamp (Osram XBO-450) is collimated through a high purity silica cell located in the LINAC beam path. Two high intensity monochromators (Bausch and Lomb) are used for wavelength discrimination and together span an accessible spectral range from 240 nm to 720 nm. The presence of light-absorbing radiolysis products in the cell was detected by a concomitant decrease in photomultiplier output. The kinetics of formation or disappearance of short-lived chemical species were quantitatively examined by means of a data analysis system shown schematically in Figure 2. The key element in this equipment is a fast transient recorder (Biomation Model 610) which digitizes and stores the incoming analog signal concurrently with an oscilloscopic display of the same information. [16]

The photoelectric detection system is operated in a region of linear response. Changes in measured light transmission at a given wavelength are related to the optical density of the target material and, by application of the Beer-Lambert law, to the concentration of absorbing species in the cell. Transient absorption spectra were constructed point by point from photographs of oscilloscopic traces or from the digitized kinetic data, recorded at several wavelengths. The time resolution of the

recording equipment was limited by the speed of response of the amplifier and asso-

ciated signal cabling to approximately 300 nsec. Quantitative determination of kinetic
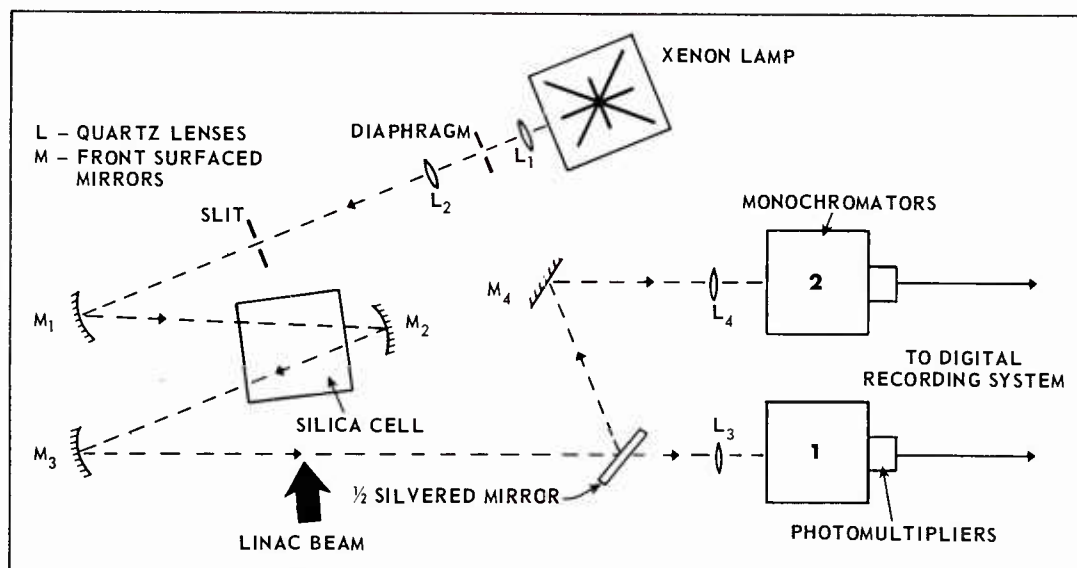

Figure 1. Basic experimental arrangement for detection of transient absorption spectra
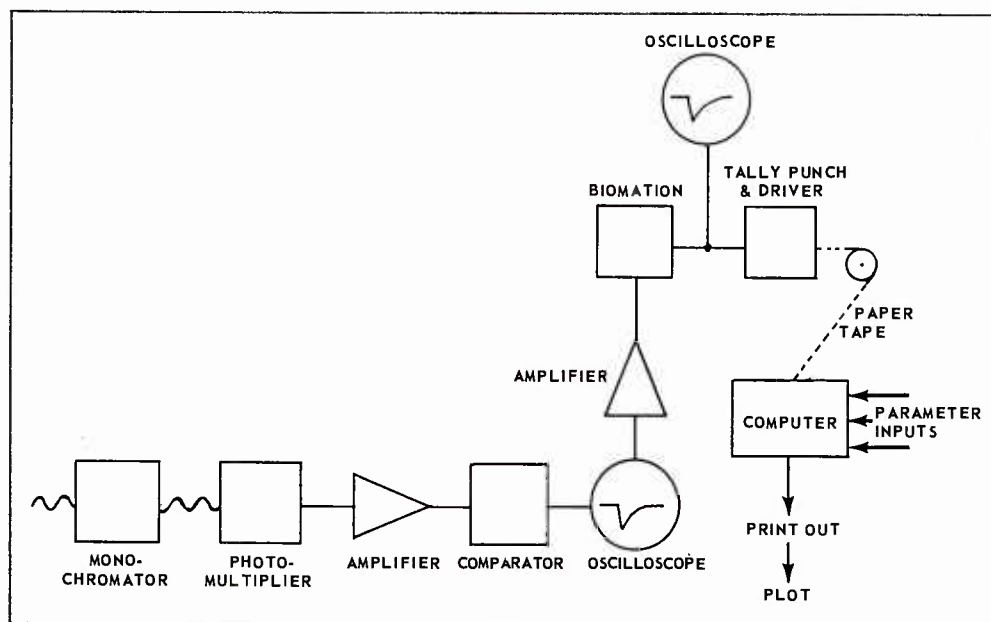

Figure 2. Kinetic absorption spectroscopy block diagram

4

behavior was therefore restricted to transients with half-lives of several microseconds or greater.

Material and methods. The apparatus used to introduce organometallic liquids into the LINAC beam is shown in Figure 3. The irradiation cell itself, of rectangular cross section 20 mm x 7 mm, was 20 mm deep along the beam axis. The design provided a reasonable compromise between small volume, to minimize cost of target material, and optical pathlength sufficient to obtain sensitive detection of transient absorptions. After a pulse, a fresh sample of liquid was pushed from the reservoir syringe to displace the irradiated material into the take-up vessel. The operation was conducted from the remote data readout area and monitored by closed circuit television. This method of filling prevented back diffusion of air into the cell and reduced the hazard to personnel from the high toxicity of some of the liquids under investigation. The reservoir syringe was filled in an air-free glove bag, after first purging with nitrogen, and transferred to the radiation area immediately prior to experimentation.

Tetraethyl silane and tetraethyl germane were purchased from PCR, Inc., tetraethyl tin from K & K Laboratories, Inc., tetraethyl lead from Research Organic/Inorganic Chemical Corporation and tetramethyl lead (80 percent in toluene) from Ventron Corporation, Alfa Products. All materials were used without further purification. They were stored refrigerated until just prior to an experiment and exposed only to the controlled atmosphere of the glove bag used for deaerating and filling procedures. Nitrogen (ultrapure grade) was passed through a Drierite column before bubbling through the compounds to remove dissolved oxygen.
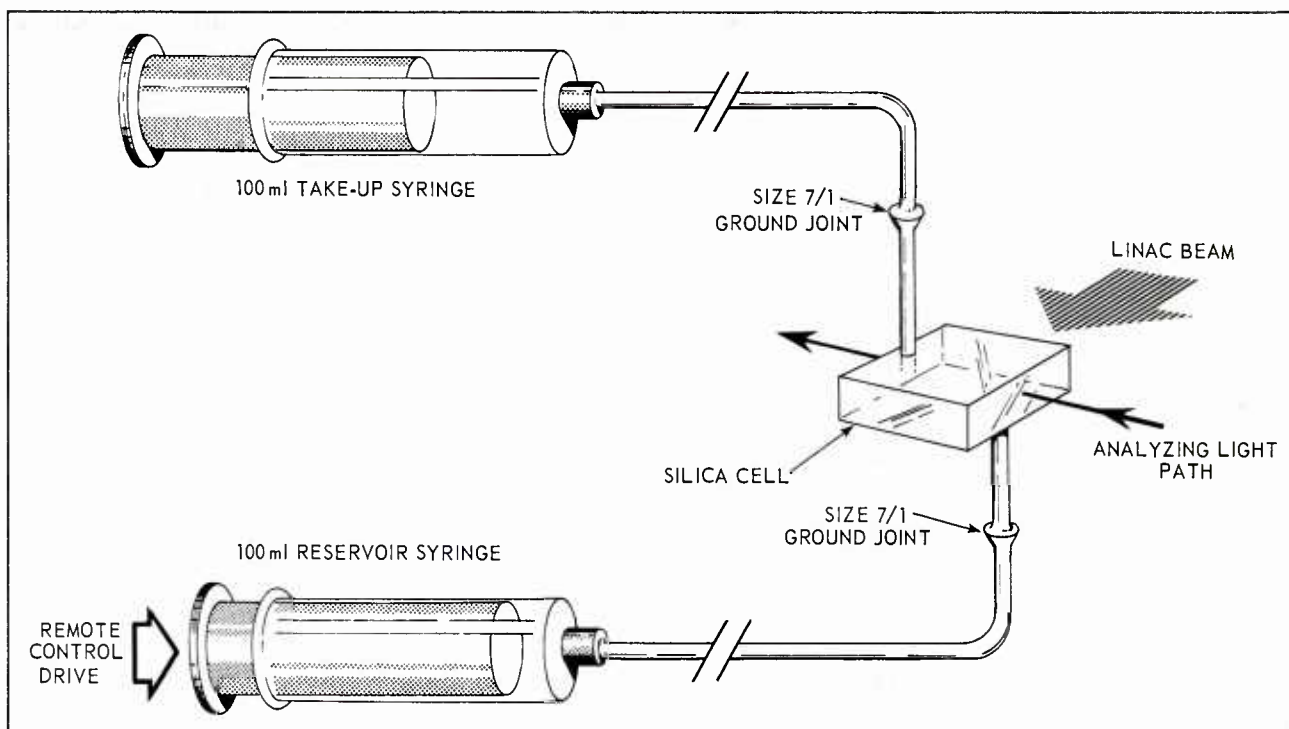
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Figure 3. Closed system for filling irradiation cell

Dosimetry. Before striking the target, the LINAC beam was broadened through a 0.06" Al scattering foil and passed through a hole in a 30-cm polybrick collimator. The cross section presented by the beam at the front face of the irradiation cell was approximately 25 mm, i.e., slightly larger than the width of the target. A Faraday cup placed in the line of sight behind the cell was used to monitor the intensity of each electron pulse. Only a portion of the total incident charge was collected; for a given target material, however, the system provided a reliable means of detecting changes in beam current delivered by the accelerator. Variations of up to $\pm$ 10 percent were accepted after normalization of Faraday cup readings to a mean value itself corresponding to a particular beam current.

6

A reasonable estimate of radiation dose absorbed by the target materials may be made by extrapolation of measurements obtained with a reliable chemical dosimeter. The aqueous ferrocyanide dosimeter[18] used for this purpose provided a means of determining dose deposited in H_2O in the same irradiation cell used for the organometallic liquids. All experiments, including dosimetry, were conducted under conditions of unchanged geometry. Prior to each experiment the LINAC was tuned to deliver through the empty irradiation cell and into the Faraday cup a beam current corresponding to that which would deposit 1030 ± 30 rads per pulse in a ferrocyanide solution.

Calculation of the electron densities of the metallic and hydrocarbon fractions of each organometallic liquid indicates that in no case is more than 10 percent of the ionization energy loss due to the metal atoms in the molecular matrix. The ionization stopping power of these materials is approximately 70 percent that of water,[1] indicating that the absorbed dose due to this particular process is lower than that delivered to water. It also may be shown that the radiation energy loss makes only a minor contribution to absorbed dose, even for those compounds containing nuclei with a large cross section for photoelectric absorption of bremsstrahlung, e.g., the lead compounds. To a first approximation, therefore, the dose absorbed by each of the liquids investigated is less than but comparable to that measured by the ferrocyanide dosimeter.

III. RESULTS AND DISCUSSION

All four tetraethyl compounds, as well as tetramethyl lead, exhibited transient absorption spectra in the visible and near ultraviolet regions following radiolysis.

7

Changes in optical absorption intensity were recorded for each material as a function of time at different wavelengths over the spectral range 290 to 620 nm. The low wavelength cut-off was somewhat higher for the substituted plumbanes because of their own increased light absorption in that region. The oscilloscope trace shown in Figure 4 is representative of the kinetic behavior of the transient absorption recorded at 334 nm in irradiated tetraethyl germane. It indicates a very rapid build-up in absorbance followed by a much slower decay, presumably to a nonabsorbing daughter product.

A complete spectrum for each compound is shown in Figure 5. The spectra were plotted from data recorded within 1 μsec of the samples receiving a 1-krad pulse. There appear to be two distinct types of spectra. The absorption bands of the tin and lead compounds exhibit well-defined shoulders which disappear within 10 μsec of a LINAC pulse. The residual absorption is much longer lived and is clearly visible after several hundred microseconds. The shorter lived transients are not seen in the spectra
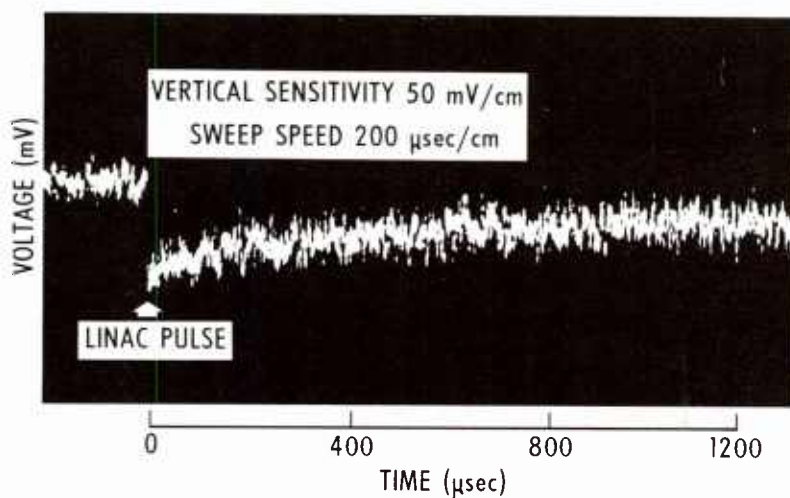

Figure 4. Decay of radiation-induced transient in $(C_2H_5)_4 Ge$ at 334 nm
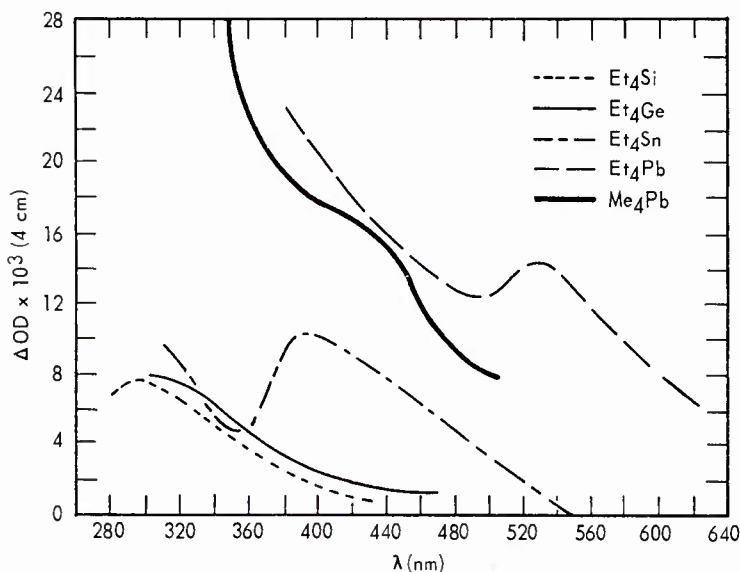
Figure 5.   Transient absorption spectra of tetra-alkyl compounds of
Group IVA elements, immediately following a 0.2-μsec
pulse of LINAC electrons

of tetraethyl silane and germane; in both cases the absorptions with maxima near 300

nm decay at a rate similar to that of the long-lived transients in the other three com-

pounds.   Time resolved spectra for each material are shown in Figure 6A-E.

The decay kinetics in the different spectral regions indicate that for the silicon

and germanium compounds the observed absorption bands can be reasonably assigned

to a single intermediate species in each case.   This species apparently decays by re-

action with its own kind or with other substrates, transient or stable, present in very

low concentration, i.e., by a second order reaction.   A graph of reciprocal optical

density versus time for the transient absorption at 334 nm in irradiated tetraethyl ger-

mane is shown in Figure 7.   The linear function is indicative of second order kinetics.

At least two intermediate species are responsible for the observed absorption

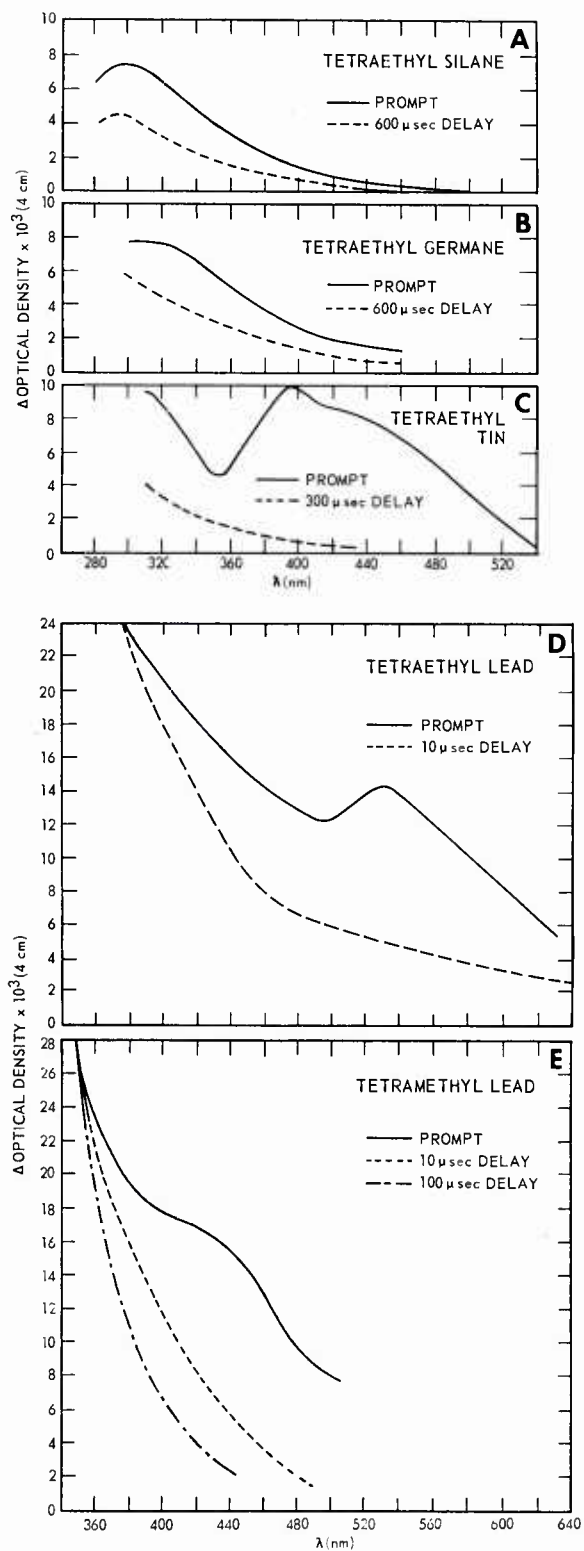bands in the lead and tin compounds.   Kinetic analysis suggests that the shorter lived

9

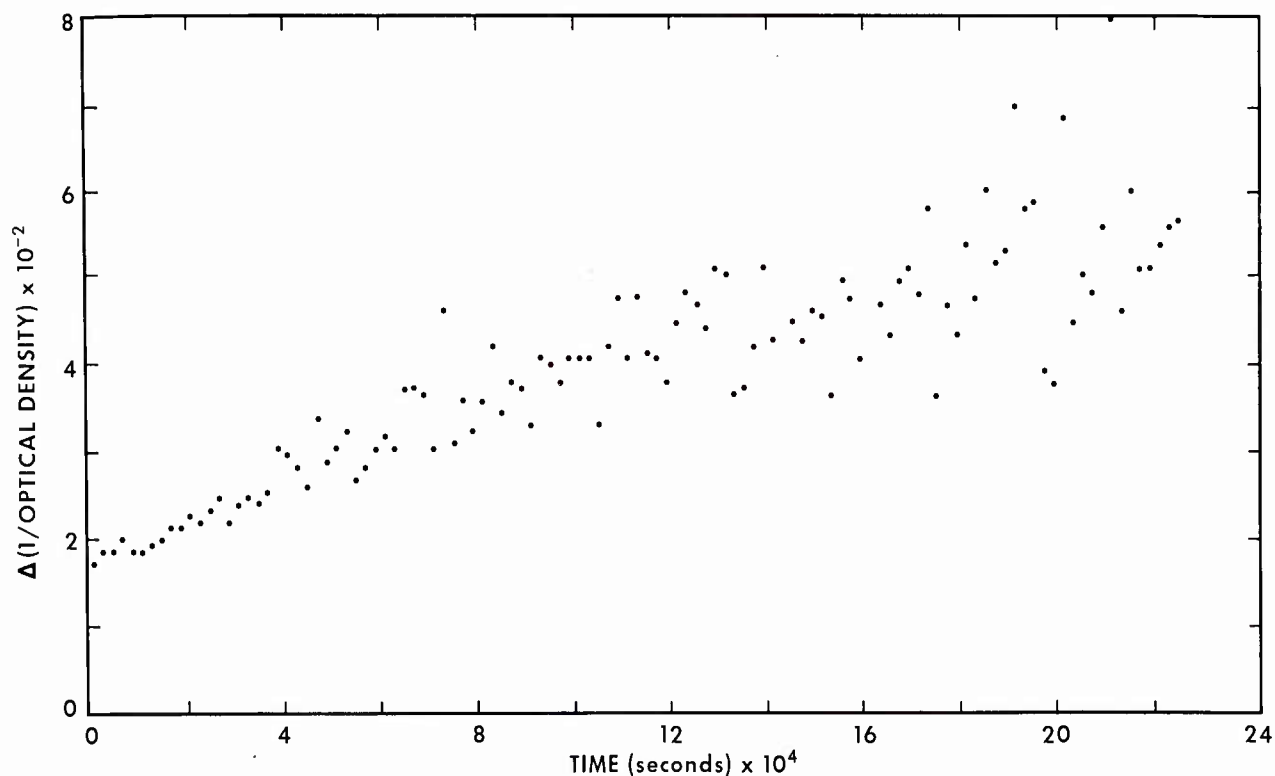Figure 6. Decay of transient absorption spectra

Figure 7. Reciprocal optical density versus time for $(C_2H_5)_4$Ge at 334 nm, for 4-cm light path cell

transient decays in each case by a first order reaction, i.e., the rate of disappearance is directly proportional to its concentration alone. If this is indeed the situation, the transient is reacting with the parent compound or undergoing unimolecular decomposition. The kinetic order of the decay of the long-lived intermediates cannot be determined, but when the data are plotted as in Figure 7 there is some deviation from linearity, indicating the presence of competing reactions in these unstable systems.

It is reasonable to assume that an important radiolytic reaction for all members of this tetra-alkyl series will be

$$(C_2H_5)_4M \longrightarrow\hspace{-0.5em}\text{\tiny\lightning}\hspace{-0.5em}\longrightarrow (C_2H_5)_3M\cdot + \cdot C_2H_5 \tag{1}$$

11
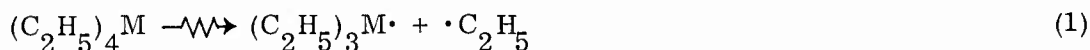
where M represents the Group IVA element. The products of radiolysis of liquid dimethyl-diethyl tin[8] and tetramethyl and tetraethyl tin[7,8] are those anticipated if the trialkyl-tin free radical produced by reaction (1) is a major initial intermediate. A possible reaction scheme in irradiated tetraethyl tin is:

$$(C_2H_5)_4Sn \xrightarrow{\hspace{0.5cm}} (C_2H_5)_3Sn\cdot + \cdot C_2H_5 \tag{2}$$

$$(C_2H_5)_4Sn + \cdot C_2H_5 \longrightarrow (C_2H_5)_3Sn(\underset{\cdot}{C}_2H_4) + C_2H_6 \tag{3}$$

$$(C_2H_5)_3Sn(\underset{\cdot}{C}_2H_4) \longrightarrow (C_2H_5)_3Sn\cdot + C_2H_4 \tag{4}$$

$$2(C_2H_5)_3Sn\cdot \longrightarrow (C_2H_5)_3Sn\,Sn(C_2H_5)_3. \tag{5}$$
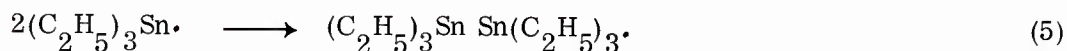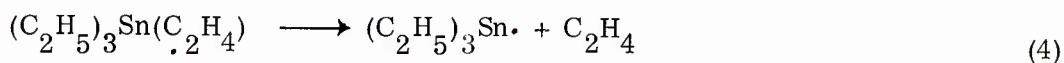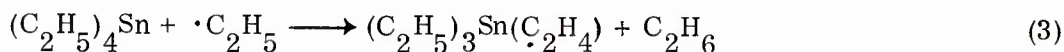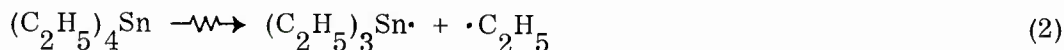
Stable radiolysis products observed by Höppner[8] in his investigation of tetra-ethyl tin included ethane, ethylene, butane and the di-tin compound (reaction (5)).

There is strong evidence that this mode of decomposition is favored in the photolysis of tetra-alkyl tin compounds.[3-5,19] Cleavage of the Sn-C bond appears to be the principal photolytic process in the gas phase. Similar investigations of the photolysis and pyrolysis of corresponding silicon and germanium compounds indicate that a simple scheme such as the one outlined above can be used to interpret many of the experimental observations. It is therefore suggested that the slowly decaying absorption bands seen in all the materials under examination be assigned to the trialkyl metal radical. The kinetic data can then be interpreted in terms of a dimerization reaction such as (5).

One possible explanation for the appearance of the short-lived transient in irradiated tetraethyl tin as well as tetramethyl and tetraethyl lead would be the

12

production of an optically excited state of the parent molecule, e.g.,

$$(C_2H_5)_4Pb \quad \longrightarrow \quad ((C_2H_5)_4Pb)^* . \tag{6}$$

When tetraethyl tin is saturated with air before irradiation, the rapidly decaying

shoulder is not visible. There appears to be little effect, if any, upon the intensity

and kinetics of disappearance of the long-lived absorption as shown in Figure 8. It

is interesting to speculate on the role of oxygen in these irradiated liquids. Oxygen

is an efficient quenching agent for triplet states and may indeed be acting as such in

tetraethyl tin, thereby removing the species or its precursor responsible for the short-

lived transient absorption.
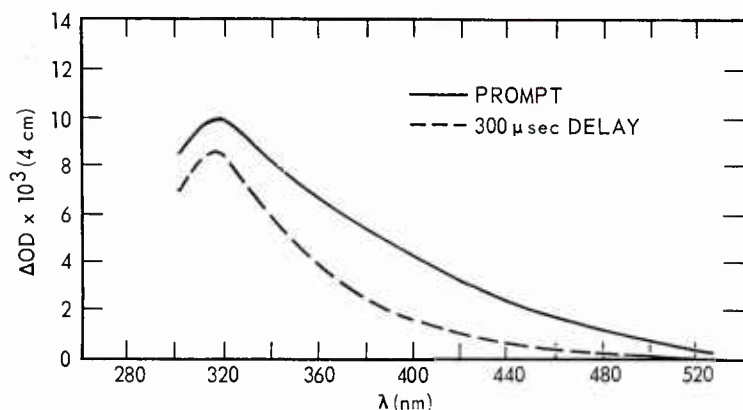
Figure 8.
Effect of oxygen on transient
absorption spectra of tetra-
ethyl tin

The photolytic decomposition of tetra-alkyl tin compounds is accelerated in the

presence of air. [13] Such an observation is not in line with the idea of the intervention

of an excited state in the radiolytic process as outlined above. The normal fate of such

an excited state in the presence of a suitable reactant would be deactivation to the

ground state, i.e., a protective effect would be operable.

Another possibility might be the formation of a dialkyl derivative, viz:

$$(C_2H_5)_4Sn \quad \longrightarrow \quad (C_2H_5)_2Sn: + 2 \cdot C_2H_5 \tag{7}$$

13
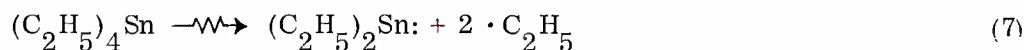
followed by rapid insertion into the Sn–C bond of a parent molecule:

$$(C_2H_5)_2Sn: \; + (C_2H_5)_4Sn \longrightarrow (C_2H_5)_3Sn \, Sn(C_2H_5)_3. \tag{8}$$
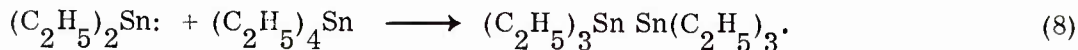
Dialkyl intermediates such as the one postulated above are believed to be involved in reactions between dichlorodimethyl silane and sodium or potassium in the gas phase.[20] Such a biradical can also be considered a triplet state.

Tetra-alkyl lead compounds are notoriously unstable when subjected to heat or photon radiation. Pyrolysis and photolysis studies[17, 21] of these materials in the gas phase indicate that dimerization of trialkyl lead radicals is negligible, whereas lead and hydrogen appear to be major products. There is an induced chain decomposition of tetramethyl lead when it is irradiated with x rays at $4^{o}K$ and then warmed to $40^{o}K$.[9] Metallic lead is also one of the products. This material has previously been suggested as a dosimeter[14] although no practical application appears to have been made.

In the present work there was no observable effect of a single pulse of electrons upon either tetraethyl or tetramethyl lead, other than the noted transient spectra. Prolonged exposure of a sample to the analyzing light of wavelength <300 nm, however, did result in opacity. A similar observation was made for the tin compound.

IV. CONCLUSIONS

The primary objective of this investigation was to determine whether or not organometallic compounds of certain Group IVA elements exhibit, upon exposure to ionizing radiation, transient absorption spectra which might be used to measure absorbed dose. This has been achieved; the course of the radiolytic process in every material examined may be observed in a readily accessible region of the spectrum. The optical density of each irradiated liquid is directly related to both G-value

14

(radiation yield of product expressed as molecules per 100-eV energy input) and the extinction coefficient of the light absorbing species. Although absolute numerical values cannot be assigned to these separate quantities at this time, the liquids in question may still be developed as dosimeters for low-energy x rays. For this purpose it would be necessary to determine the relationship between optical density and absorbed radiation dose as measured by a primary dosimeter, e.g., a calorimeter, over a predetermined range of x-ray energies.

The scope of this study was such that it is not possible to define the degree of time resolution achievable in such a dosimeter. If the lifetime of a transient species can be sufficiently reduced by addition of a suitable reactant to the target material, e.g., effect of added acid in the aqueous e_{aq}^- dosimeter,[10] it may be possible to monitor the profile of a radiation pulse with a rise and fall time of several nanoseconds. Further experimentation to examine this possibility would be conducted along the lines of the current investigation, using the LINAC as the pulsed radiation source. An extensive modification of the photoelectric detection system would be required, however, to attain the necessary time response.

This investigation has dealt with some of the initial free radical reactions occurring in irradiated tetra-alkyl compounds of Group IVA metals following their exposure to short intense pulses of high-energy electrons. Determination of the time scale of these processes has been made possible as a result of direct measurements of the light absorbing properties of the reactants. It appears that rupture of a metal-carbon bond, giving rise to a trialkyl metal radical, is a major radiolytic process in all

cases. The data also indicate that for tetraethyl lead and tin, other free radicals are involved in the formation of radiation products. Further experimental work will be required if these short-lived intermediates are to be identified. The present study meanwhile has yielded new and valuable information on the nature of radiolytic mechanisms in this class of compounds.

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APPENDIX A

A spectrometry system for high intensity x-ray fields, based on pulse radiolysis in organometallic liquids, would consist of a series of optical cell-pairs. Each of the cells of a pair would contain a different organometallic and each pair would respond most strongly to photons with energies between the K-edges of the cell fluids. Thus, by choosing appropriate organometallics as cell fluids, the energy spectrum of the x-ray field could be covered.

As an illustrative example the response function for a cell-pair containing tin and iodine will be calculated. These materials were chosen because tetraethyl tin is one of the compounds studied in the experiment described in this report, and iodine because the K-edge is appropriately located with respect to the tin K-edge, and iodine readily forms organic compounds.

Each cell-pair would be used with a K-edge filter of the same material as the higher Z cell fluid material, in this case, iodine. The energy spectrum of transmitted photons is given by $D(E) = S(E)e^{-\mu(E)x}$, where $S(E)$ is the spectrum of photons in the x-ray field, $\mu(E)$ is the total photon cross section of iodine, and x is the filter thickness. For this calculation $S(E)$ was arbitrarily chosen to be Gaussian-like in shape, to peak at 40 keV, and to drop to 0.01 of peak at 0 and 80 keV. The distribution is given by $S(E) = 50 \exp-[(E-40)^2/(18.7)^2]$. Figure A-1 shows this distribution as well as the total photon cross sections for tin and iodine, in cm^2/g.

The response functions are given by $R(E) = D(E)[1-\exp-(\mu(E)t)]$, where $\mu(E)$ is the total photon cross section for either tin or iodine, and t is the thickness of a cell. The cell thicknesses for this calculation were chosen such that their energy absorptions
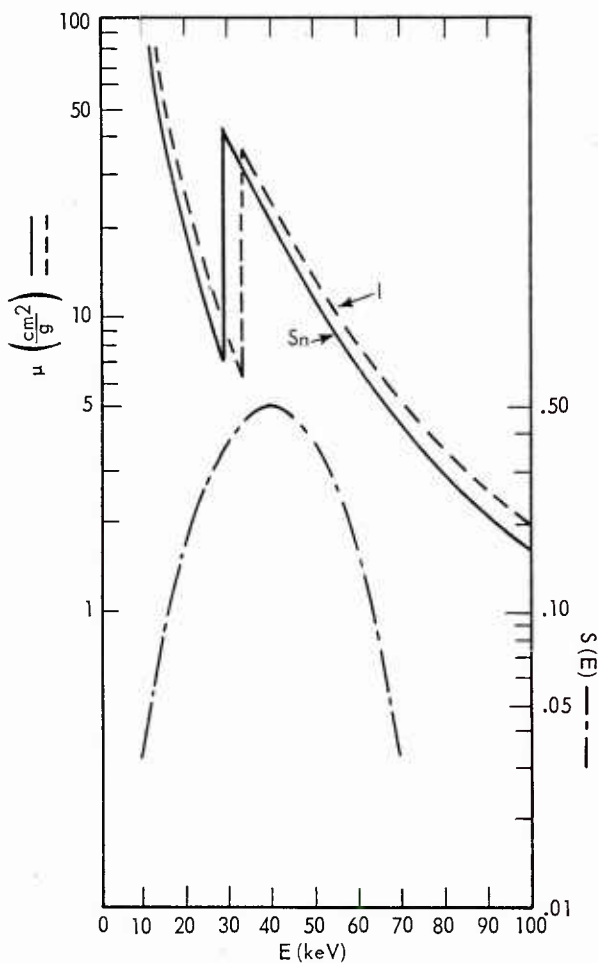
19

Figure A-1.
Total photon cross sections for tin and
iodine and x-ray field spectrum, S(E)

were the same at 33.2 keV. In this way energy absorption in the two cells is made

nearly the same for photons below 29.2 and above 33.2 keV in energy. Between these

values, the tin cell absorbs strongly, because D(E) peaks just above the tin K-edge,

while the iodine cell absorbs weakly because D(E) peaks just below the iodine K-edge.

Thus, the total cell-pair response function, i.e., the difference of the two response

functions, is due almost entirely to photons with energies between 29.2 and 33.2 keV.

Fundamentally, this is the way each cell-pair will work. By using a K-edge filter of

the same material as the higher Z cell material, the transmitted spectrum will always

20

peak just below the higher Z K-edge and just above the lower Z K-edge.   Figure A-2

shows (A) the transmitted photon spectrum D(E);   (B) the tin cell response function

$R_{Sn}(E)$;   (C) the iodine cell response function $R_I(E)$;   and (D) the difference
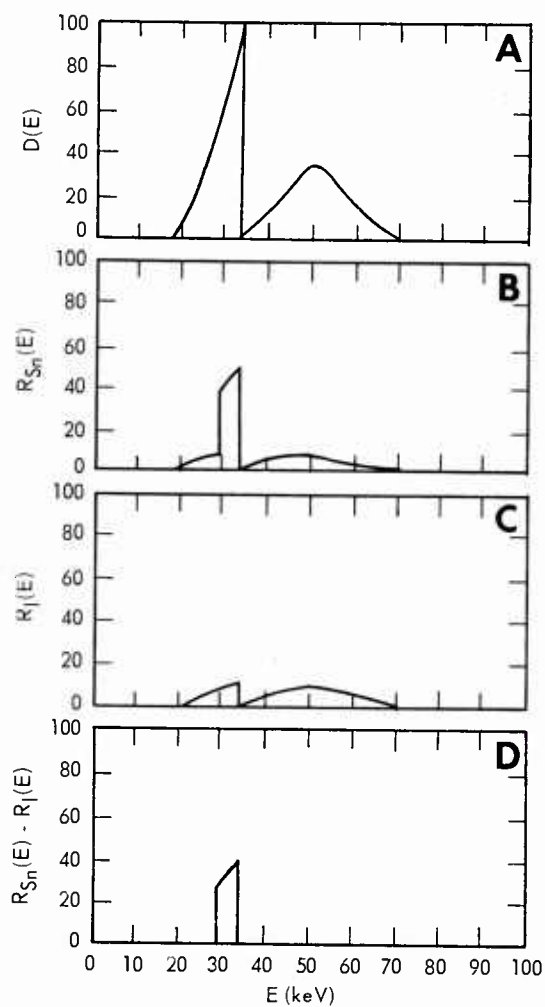
$R_{Sn}(E) - R_I(E)$.

Figure A-2.
(A) Transmitted photon spectrum, D(E);
(B) Tin cell response function; (C) Iodine
cell response function; (D) Total response
function, $R_{Sn} - R_I$

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13. ABSTRACT

The methods of kinetic optical spectroscopy have been employed to observe the formation
and decay of short-lived transients produced by pulse radiolysis of the tetra-alkyl compounds
of the Group IVA metals. Time resolved transient spectra over the range of 290 nm to 620 nm
are presented. The probable mechanisms of the radiation-induced molecular disruption are
considered and the feasibility of utilizing these compounds as dosimeters in the low-energy
x-ray region is discussed.

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